Synthesis of ZnO- Al₂O₃-Cr₂O₃ System Pigments with CrCl₃

Soo-Nyong Choi† and Byung-Ha Lee

Department of Materials Science & Engineering, Myongji University, Yongin 449-728, Korea

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ABSTRACT

The coloring agents Cr₂O₃ and CrCl₃ were manipulated in this study to synthesize ZnO-Al₂O₃-Cr₂O₃ system pigments by changing their mixing ratio. The addition of varying amounts of mineralizer was also tested to obtain better color development of the pink pigment. In the synthesis of ZnO-Al₂O₃-Cr₂O₃-CrCl₃ pigments, the best composition is Cr₂O₃-0.1 mole and CrCl₃-0.2 mole when Cr₂O₃ is partially substituted with CrCl₃ to synthesize them. Among the ZnAl₁ₓCr₁₋ₓO₃ compositions to which a mineralizer was not added, ZnO-1 mole, Al(OH)₃-1.7 mole, Cr₂O₃-0.075 mole, and CrCl₃-0.15 mole showed a desirable pink hue. The measurements of pigments L*, a* and b*, were L* 81.81, a* 16.65 and b* 0.45, and when the synthesized pigments were applied to a zinc glaze, the measurements were L* 60.41, a* 28.39, and b* 16.97. When adding a mineralizer, a 2 wt% addition resulted in the most favorable pink color. The composition for the most favorable result that included a mineralizer was Al(OH)₃-1.8 mole, Cr₂O₃-0.05 mole, and CrCl₃-0.1 mole, and the calcination temperature was 1250°C. The pigment color analysis showed L* 82.52, a* 17.14 and b* -1.18, and the measurements of L*, a* and b* in the glaze were L* 60.97, a* 28.77 and b* 13.72.

Key words: CrCl₃, Pigment, Pink color, Mineralizer

1. Introduction

Cr₂O₃ develops various colors like pink, red, redish-brown or green when used in ceramic pigments. The seed crystal turns red in the structures that have of 6-coordinated oxygen atoms with the strong bonding force in the red inorganic pigment having Cr as a color source. Oxides with 6-coordinated oxygen atoms include corundum, spinel, sphene, ilmenite and perovskite.³

Pigments were once named or categorized by their color formation mechanism or use; now, however, the Dry Color Manufacturers’ Association (DCMA) system is used to categorize 51 pigments into 14 categories.²,³

The DCMA system classifies pigments based on their crystal structure. In the system, spinel is assigned to category XIII, in which there are 20 kinds of pigments. For instance, chrome alumina pink corundum (DCMA 3-03-5), chrome alumina pink spinel (DCMA 13-32-5), chrome titan pink sphene (DCMA 12-25-5) and chrome iron black spinel (DCMA 13-50-9) belong to category XIII.²,³

In order to synthesize chrome alumina pink spinel, this study conducted an experiment replacing a part of Cr₂O₃ with CrCl₃ in the composition of ZnAl₁ₓCr₁₋ₓO₃,⁵ the best formula for pink pigment thus far developed. In a further attempt to produce a superior pink pigment, the composition was changed to ZnAl₁₋ₓCr₁₊ₓO₃ by adding a mineralizer:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cr₂O₃</th>
<th>Al(OH)₃</th>
<th>CrCl₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>1.8</td>
<td>0.1</td>
</tr>
<tr>
<td>B</td>
<td>1.6</td>
<td>0.7</td>
<td>0.09</td>
</tr>
<tr>
<td>C</td>
<td>1.6</td>
<td>0.05</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 1. Composition of Samples A, B, C

2.1. Pigment Mixture

In order to synthesize a chrome alumina pink pigment in which Cr is solved, ZnO, Al(OH)₃ (Junsei, Japan, chemical pure), Cr₂O₃ and CrCl₃ (Duksan, Korea) were used as starting materials, and H₂BO₃ (Duksan, Korea) was used as a mineralizer. Results indicate that the maximum solid solution limit of Cr₂O₃ for synthesizing a pink pigment is 0.2 mole;² based on this, Cr₂O₃ was partly replaced with CrCl₃ in this experiment. The chemical compositions used in this experiment are described in Table 1.

Table 2 shows the result of the experiment varying the substitution amount of the coloring oxide, Cr₂O₃, based on the optimal result from Table 1.

To synthesize the pigments, two different one-hour calci-

Table 1. Composition of Samples A, B, C

<table>
<thead>
<tr>
<th>Samples</th>
<th>ZnO</th>
<th>Al(OH)₃</th>
<th>Cr₂O₃</th>
<th>CrCl₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>1.8</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>1.6</td>
<td>0.7</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1.6</td>
<td>0.05</td>
<td>0.8</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Composition of Samples
Table 3. Composition Adding Increment of \( \text{H}_3\text{BO}_3 \)

<table>
<thead>
<tr>
<th>Samples Materials</th>
<th>HB1</th>
<th>HB2</th>
<th>HB3</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( \text{Al(OH)}_3 )</td>
<td>1.8</td>
<td>1.7</td>
<td>1.6</td>
</tr>
<tr>
<td>( \text{Cr}_2\text{O}_3 )</td>
<td>0.05</td>
<td>0.075</td>
<td>0.1</td>
</tr>
<tr>
<td>( \text{CrCl}_3 )</td>
<td>0.1</td>
<td>0.15</td>
<td>0.2</td>
</tr>
<tr>
<td>( \text{H}_3\text{BO}_3 )</td>
<td>1, 2, 3 wt%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns of samples synthesized at 1300°C/1 h.

Table 3 displays the compositions to which 1 wt%, 2 wt% and 3 wt% of the mineralizer \( \text{H}_3\text{BO}_3 \) were added in order to further elevate reactivity and obtain a superior pink coloring.

2.2. Analysis of the Characteristics and Color Development of the Pigments

To examine the creation of the crystalline phases of the calcined pigments, X-ray diffraction (XRD) (XRD-7000, Shimadzu, Japan) analysis was performed, and SiO\(_2\) was used as standard substance. To analyze the solid solution relationship and amorphous materials of the crystalline phases in the synthesized pigments, a Fourier transform infrared spectroscopy (FT-IR) (IR Prestige-21, Shimadzu, Japan) analysis was conducted. The range of measurement was 300 cm\(^{-1}\) to 2000 cm\(^{-1}\), and the resolution was set as 16 cm\(^{-1}\). For measuring the color and reflection rate of the pigments, a UV-vis spectrometer (UV-2401PC, Shimadzu, Japan) was used. To examine the color development of the pigments in the glaze, 8 wt% of the synthesized pigments was added to the zinc glaze separately. The specimens were made of white porcelain, and the glazed specimens were calcined at 1250°C in an electric furnace for thirty minutes and were cooled naturally. The Seger formulas of the glazes used are shown below.

\[
\begin{align*}
\text{Zinc glaze} & : 0.1469 \text{KNaO} 0.2215 \text{Al}_2\text{O}_3 1.6557 \text{SiO}_2 \\
& 0.3802 \text{CaO} 0.0089 \text{MgO} \\
& \text{pigments} 8 \text{wt% (1)} \\
& 0.4540 \text{ZnO}
\end{align*}
\]

3. Results and Discussions

3.1. XRD Analysis

Composition A, which contains a large amount of \( \text{CrCl}_3 \), showed \( \text{Al}_2\text{O}_3 \) and the spinel phase, and it is thought that this resulted from the volatilization of the \( \text{CrCl}_3 \). Composition B consists of \( \text{Cr}_2\text{O}_3 \) and \( \text{CrCl}_3 \) in the ratio of 1:1, and composition C has a large amount of \( \text{Cr}_2\text{O}_3 \). In compositions B and C, the single spinel phase was observed. Fig. 1 is the result of XRD measurement on the pigment synthesized at 1300°C for one hour in the composition shown in Table 1.

B was the better of compositions B and C, and had a ratio of \( \text{Cr}_2\text{O}_3 \) to \( \text{CrCl}_3 \) of 1:1. In composition A, calcined at 1250°C, the character bands of \( \text{Al}_2\text{O}_3 \) appeared at 359 cm\(^{-1}\), 506 cm\(^{-1}\), and 700 cm\(^{-1}\) (dotted lines), which concurs with the
result of XRD analysis. In both compositions B and C, the character bands of spinel developed at 347 cm⁻¹, 371 cm⁻¹, 414 cm⁻¹, 460 cm⁻¹, 514 cm⁻¹, 917 cm⁻¹, and 700 cm⁻¹ (full lines), while the character bands of spinel appeared at 346 cm⁻¹ and 372 cm⁻¹ (○) in only composition B, which indicates that composition B has the optimal composition ratio of Cr₂O₃ and CrCl₃. When calcination was conducted at 1300°C, the reactivity of the spinel character band increased more. In composition C, which has a large amount of Cr₂O₃, as calcination temperature became higher, surplus character bands of Cr₂O₃ were seen at 304 cm⁻¹, 337 cm⁻¹ and 411 cm⁻¹. The difference between B and C could not be identified through XRD analysis; therefore, FT-IR measurement was applied, with the results shown in Fig. 2.

The single spinel phase was observed in every composition. The crystalline phases of the pigment were seen more when Cr₂O₃ and CrCl₃ were used rather than when Cr₂O₃ was used alone. This is thought to have resulted from the effect of CrCl₃ with was highly active. Fig. 3 shows the result of XRD measurement on the pigment synthesized using the composition shown in Table 2 where the Cr₂O₃ content was altered in the spinel composition (composition B).

As a sample specimen, the d value of the SiO₂ (1 0 1) side was set as a criterion. Consequently, as Al₂O₃ was replaced by Cr₂O₃, the d value of the calcined pigment increased, and Al became substituted with Cr. The d value calculated using the result of the XRD analysis shown in Fig. 2 is presented in Fig. 4.

XRD analysis showed only the single spinel phase. In the cases of HB1 and HB3 where 0.1 mole and 0.2 mole of Cr₂O₃ in spinel were replaced, the added amount of the mineralizer was increased and the half width of XRD was decreased, but the half width of XRD was tended to increase when the added amount of mineralizer reached 3%. However, when 0.15 mole of Cr₂O₃ was substituted, the value was consistent regardless of the amount of mineralizer added. Accordingly, the optimal addition of mineralizer was 2 wt%, and the optimum pigment composition was HB2. Fig. 5 presents the values of full width at half maximum in order to examine crystallinity after the pigment structured in the composition shown in Table 3 was calcined at 1250°C.

### 3.2. FT-IR Analysis

An FT-IR analysis was conducted to check for non-reactive Cr₂O₃ not observed in the XRD measurement.

Character bands (full lines) appeared at 340 cm⁻¹, 360 cm⁻¹, 400 cm⁻¹, 465 cm⁻¹, 524 cm⁻¹, 624 cm⁻¹, 750 cm⁻¹, and as
calcination temperature became higher, the intensity of the spinel character band increased, too. It is thought that the simultaneous use of \( \text{Cr}_2\text{O}_3 \) and \( \text{CrCl}_3 \) improved the crystal-line phase, and this was also verified in the calculation of full width at half maximum. In CB3, the composition with a small amount of \( \text{Al}_2\text{O}_3 \), the character bands of \( \text{Cr}_2\text{O}_3 \) appeared distinctly at 367 cm\(^{-1}\), 408 cm\(^{-1}\), 454 cm\(^{-1}\), 507 cm\(^{-1}\) and 609 cm\(^{-1}\), and it is thought that as the spinel crystal was partly dissolved, the character bands of \( \text{Cr}_2\text{O}_3 \) became visible.\(^6\)

Spinel character bands were shown at 345 cm\(^{-1}\), 371 cm\(^{-1}\), 464 cm\(^{-1}\), 524 cm\(^{-1}\), 578 cm\(^{-1}\) and 619 cm\(^{-1}\) (full lines). As more mineralizer was added, the reactivity of the spinel character bands became higher. In the composition to which 1 wt\% of mineralizer was added, as calcination temperature increased, the intensity of the spinel character band at 346 cm\(^{-1}\) became higher, too. In HB2, the composition with more \( \text{Cr}_2\text{O}_3 \), the intensity of the spinel character band (full line) was highest. However, as character bands with surplus \( \text{Cr}_2\text{O}_3 \) started to appear at 362 cm\(^{-1}\), 417 cm\(^{-1}\), 454 cm\(^{-1}\), 508 cm\(^{-1}\) and 609 cm\(^{-1}\) (dotted lines), the spinel character band became even higher in composition HB3.\(^8\) In composition HB1 with 2 wt\% mineralizer added, the spinel character band at 340 cm\(^{-1}\) was the best. For that composition, the \( \text{Cr}_2\text{O}_3 \) content was 0.05 mole, and the synthetic temperature was 1250°C. As calcination temperature and \( \text{Cr}_2\text{O}_3 \) content increased, surplus \( \text{Cr}_2\text{O}_3 \) was shown at 348 cm\(^{-1}\), 413 cm\(^{-1}\), 508 cm\(^{-1}\), and 608 cm\(^{-1}\) (dotted lines). Moreover, the spinel character band at 633 cm\(^{-1}\) (full line) moved to 603 cm\(^{-1}\) as the \( \text{Cr}_2\text{O}_3 \) content increased; thus, it can be seen that Al was replaced by Cr. When 3 wt\% mineralizer was added, the spinel character band at 340 cm\(^{-1}\) was weak, and spinel bands at 700 cm\(^{-1}\) and 756 cm\(^{-1}\) (full lines) were strong. \( \text{Cr}_2\text{O}_3 \) character bands at 348 cm\(^{-1}\), 413 cm\(^{-1}\), 508 cm\(^{-1}\), and 608 cm\(^{-1}\) (dotted lines) were stronger than when 1 wt\% or 2 wt\% mineralizer was added. Accordingly, when 2 wt\% mineralizer was added, the spinel character band at 340 cm\(^{-1}\) was the strongest. When 2 wt\% mineralizer was added, and \( \text{Al}_2\text{O}_3 \) was partly substituted with \( \text{Cr}_2\text{O}_3 \), the optimal substitution amount was 0.05 mole, and the calcination temperature was 1250°C. Fig. 7 shows the compositions to which 1 wt\%, 2 wt\% and 3 wt\% of mineralizer were added.

3.3. UV-Vis. Spectroscopy

The \( a' \) value was highest in composition B with \( \text{Cr}_2\text{O}_3 \)-0.1 mole and \( \text{CrCl}_3 \)-0.2 mole. When applying the synthesized pigment to zinc glaze, the \( a' \) value was also high. Fig. 8 shows the result of color measurement on the pigments calcined at 1250°C and 1300°C for the compositions shown in Table 1.

In composition CB1, with a large amount of \( \text{Al(OH)}_3 \), the absorption band at 431 nm contributing to the development of pink showed lowest intensity. According to the color analysis results, \( a' \) was low whereas \( b' \) was high; thus, a yellowish pink color developed. The composition with the best development of pink color was CB2, which was calcined at 1300°C. In composition CB3, the \( \text{Al(OH)}_3 \) content was lower while the \( \text{Cr}_2\text{O}_3 \) content was higher, so the 542 nm band moved a little toward the long wavelength. It is also inferred that the improvement of 686 nm band intensity.
made the pink color deeper. According to the Tanabe-Sugano theory, 542 nm is a chief band for developing pink, and 686 nm is a character band of Cr(III).

Fig. 9 shows the result of UV-vis. measurement on the pigments calcined at 1250°C and 1300°C for the compositions shown in Table 2.

Color development was most favorable in compositions for which Al(OH)₃ content was 1.7 mole, Cr₂O₃-0.075 mole, or CrCl₃-0.15 mole. The L*, a*, and b* value of the pigment were L* 81.81, a* 16.65, and b* 0.45, and the result of applying it to glaze was L* 60.41, a* 28.39, and b* 16.97. The pigment containing both Cr₂O₃ and CrCl₃ developed a clearer pink in terms of the pigment and glaze color than was developed by the pigment using Cr₂O₃ alone. Fig. 10 shows the result of the pigments calcined at 1250°C and 1300°C and the pigment calcined at 1250°C in an electric furnace for 30 min after adding 8 wt% of the pigment to zinc glaze.

When Cr₂O₃ and CrCl₃ were used together rather than when Cr₂O₃ was used alone, peak intensity change was greater; therefore, it can be seen that CrCl₃ accelerated reactivity and affected color development. When 2 wt% mineralizer was added, the pink pigment showed an optimal effect. When 2 wt% mineralizer was added, the Al(OH)₃ content was 1.8 mole, and the synthetic temperature was 1250°C. The color analysis showed the same result. Fig. 11 presents the result of UV-vis measurement on pigments from among the ZnO-
Fig. 10. CIE L*, a*, b* colorimetric parameters of pigments and glazed samples fired at 1250°C, 1300°C/1 h. (without mineralizers)

Fig. 11. UV-vis spectra of synthesized pigments HB1-HB3 added mineralizer (2 wt%) synthesized at 1250°C, 1300°C/1 h.

Fig. 12. CIE L*, a*, b* colorimetric parameters of pigments and glazed samples fired at 1250°C/1 h. (with mineralizers)
Al(OH)$_2$-Cr$_2$O$_3$-CrCl$_3$ compositions with 2 wt% added mineralizer that were calcined at 1250°C or 800°C for one hour. The result of pigment color analysis was $L^*$ 82.52, $a^*$ 17.14 and $b^*$ -1.18. As this pigment was applied to a zinc glaze, the measurements of the glaze in terms of $L^*$, $a^*$ and $b^*$ were $L^*$ 60.97, $a^*$ 28.77 and $b^*$ 13.72. This is presented in Fig. 12.

4. Conclusion

This study manipulated the coloring agents Cr$_2$O$_3$ and CrCl$_3$ to synthesize ZnO-Al$_2$O$_3$-Cr$_2$O$_3$ system pigments by changing their mixing ratio. Various compositions of ZnAl$_{1-x}$Cr$_{2x}$O$_3$ were tested, and the addition of varying amounts of mineralizer was also tested to obtain better color development of the pink pigment. Results are summarized below.

1. In this experiment, Cr$_2$O$_3$ was partially substituted with CrCl$_3$ to synthesize ZnO-Al$_2$O$_3$-Cr$_2$O$_3$ system pigments. In composition A, containing a large amount of CrCl$_3$, Al$_2$O$_3$ and the spinel phase were observed. Moreover, the single spinel phase appeared in composition B, which had a ratio of Cr$_2$O$_3$ to CrCl$_3$ of 1:1, as well as in composition C, which had a large amount of Cr$_2$O$_3$. According to FT-IR and color analyses on compositions B and C with the single spinel phase, synthesis of pink pigments was favorably conducted with the composition of Cr$_2$O$_3$:1 mole and CrCl$_3$:0.1 mole.

2. Among the compositions of ZnAl$_{1-x}$Cr$_{2x}$O$_3$ to which the mineralizer was added, the ones developing desirable pink color were ZnO-1 mole, Al(OH)$_2$:1.7 mole, CrCl$_3$:0.15 mole and Cr$_2$O$_3$:0.075 mole. The $L^*$, $a^*$ and $b^*$ measurements of the pigment were $L^*$ 81.81, $a^*$ 16.65 and $b^*$ 4.5, and $L^*$ 60.41, $a^*$ 28.39 and $b^*$ 16.97 when applying the pigment in a glaze.

3. When the mineralizer was added, the optimum amount of added H$_3$BO$_3$ was 2 wt%. When the mineralizer was used, the optimal composition of the pigment was Al(OH)$_2$:1.8 mole, Cr$_2$O$_3$:0.05 mole and CrCl$_3$:0.1 mole (HBO), and the synthetic temperature was 1250°C. The $L^*$, $a^*$ and $b^*$ measurements of the pigment were $L^*$ 82.52, $a^*$ 17.14 and $b^*$ -1.18, and the $L^*$, $a^*$ and $b^*$ measurements of the pigment in zinc glaze were $L^*$ 60.97, $a^*$ 28.77 and $b^*$ 13.72.

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